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Methylation of Trimethyltin Compounds by Estuarine Sediments

Abstract. Both biologically active and autoclaved sediments convert trimethyltin hydroxide to the volatile tetramethyltin. Larger amounts of tetramethyltin were formed in the bioactive sediments than in the sterile sediments. No volatile tin compounds were detected in the absence of trimethyltin hydroxide or from trimethyltin hydroxide in seawater or in seawater containing bentonite. The formation of tetramethyltin is slow, taking over 80 days at 16°C to reach a maximum. The extent of conversion, although significant, is not extensive. The formation of tetramethyltin occurs in estuarine sediments by both abiotic and biologically enhanced pathways. A redistribution mechanism accounts for at least the abiotic pathway and possibly both formation pathways.

Over 25,000 metric tons of organotin compounds are used annually throughout the world (1). A major portion of these includes the triorganotin biocides, whose use for the prevention of the fouling of ship hulls and other marine structures is continually increasing. Such use represents an important anthropogenic input of tin into the marine environment. The fate of organotins is just beginning to receive attention (2, 3).

The environmental significance of tin methylation is uncertain at present. Laboratory studies have suggested the potential for biomethylation of tin. Dizikies *et al.* (4) have reported that methylcobalamin, a vitamin B₁₂ derivative that is involved in bacterial methanogenesis, will transfer a methyl group to inorganic Sn(III). However, the tin compounds introduced into the environment are in the Sn(IV) state. It is conceivable, but not likely (5), that in highly reducing environments such as anoxic estuarine sediments some Sn(III) may be produced by the reduction of Sn(IV). Then methylation of Sn(III) species might occur.

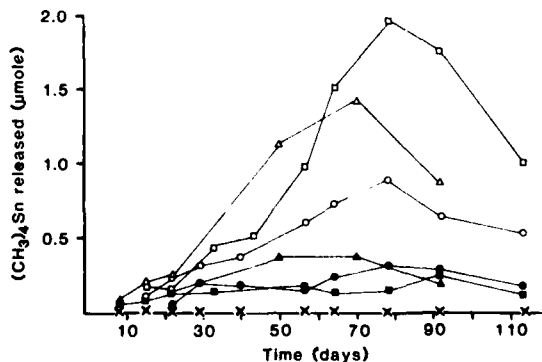
It has also been reported that methylcobalamin is capable of methylating trimethyltin acetate in a manner analogous to mercuric acetate (6), but no evidence for the formation of tetramethyltin [(CH₃)₄Sn] was presented. Huey *et al.* (7) observed the methylation of inorganic and monomethyltin by a *Pseudomonas* sp. from Chesapeake Bay. Recently inorganic tin(IV), mono-, di-, and trimethyltin compounds have been detected in the water of Tampa Bay (8), the water of Lake Michigan (9), and human urine (8). These compounds could have been produced by an environmental methylation of tin, as suggested by Craig (3). To our knowledge, no evidence regarding environmental methylation of trialkyltin compounds has been presented.

Our investigations were carried out to determine the potential for environmental methylation of trialkyltin(IV) species. Trialkyltins, including hexabutyldistannoxane and tributyltin fluoride, are the most frequently used organotins for the control of biofouling and represent major inputs of organotins into estuarine eco-

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Fig. 1. The amount of (CH₃)₄Sn in the headspace, as a function of time, formed during the incubation of (CH₃)₃SnOH in sediment (○), sediment plus Na₂S (□), sediment plus sodium acetate (Δ); solid symbols represent the corresponding autoclaved controls; x represents seawater, bentonite, and all flasks without added (CH₃)₃SnOH.



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systems. We selected trimethyltin hydroxide $[(CH_3)_3SnOH]$ as a model compound for initial studies since the product, $(CH_3)_4Sn$, is volatile, insoluble in water, and easily analyzed in the headspace over the sediment-water phase.

Anoxic estuarine sediments were obtained from the tidal flats near Alameda, California (in San Francisco Bay), and were composed of a sandy silt rich in organic matter. To triplicate 250-ml flasks containing 100 ml of seawater and 100 ml of sediment, either 0.30 g of sodium acetate, 15 mg of sodium sulfide ($Na_2S \cdot 9H_2O$), or nothing (in the case of the sediment controls) was added. A fourth set of flasks contained only 200 ml of seawater, and a fifth set contained 25 g of bentonite (a reference clay) and 160 ml of seawater. One flask from each set was autoclaved at 121°C for 40 minutes. Then $(CH_3)_3SnOH$ (15 mg) was added to the autoclaved flasks after cooling to room temperature and to one of the nonautoclaved flasks from each set. No organotin was added to the second nonautoclaved flask. All flasks were capped with Twistit stoppers with the twist-off nipples intact and incubated statically at 16°C.

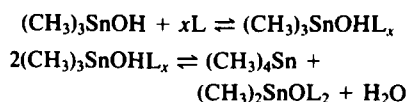
Periodically, a 500- μ l headspace sample was withdrawn through the intact twist-off nipple for analysis by gas chromatography. The $(CH_3)_4Sn$ was analyzed on a flame ionization chromatograph (Varian 2400) with a 1.5 percent OV-101 on H/P Chromasorb G column (Varian Associates), identified by a comparison of the retention time with that of authentic $(CH_3)_4Sn$, and quantified by means of an external standard prepared by adding a known amount of $(CH_3)_4Sn$ to a flask containing seawater.

We observed the formation of $(CH_3)_4Sn$ in sediment samples inoculated with $(CH_3)_3SnOH$ (Fig. 1). After 80 days the active sediments had produced 2.7 times the amount of $(CH_3)_4Sn$ found in the autoclaved controls. The maximum amount of $(CH_3)_4Sn$ produced was nearly 2 μ mole or 2.4 percent of the $(CH_3)_3SnOH$ added (10). Whereas $(CH_3)_4Sn$ was produced in both sterile and active sediments, no methyltin compounds were observed in the absence of added $(CH_3)_3SnOH$. In seawater with $(CH_3)_3SnOH$ or in seawater containing bentonite and $(CH_3)_3SnOH$, no $(CH_3)_4Sn$ was formed.

The production of $(CH_3)_4Sn$ in active sediments was enhanced by added acetate and sulfide. The addition of 15 mg of $Na_2S \cdot 9H_2O$ to the sediments resulted in a doubling of the amount of $(CH_3)_4Sn$ produced, and the addition of 0.30 g of sodium acetate to the sediment produced

a 70 percent increase over the case with the sediment alone. The autoclaved sediments, with or without additional acetate and sulfide, were not significantly different in the amount of $(CH_3)_4Sn$ formed. These results demonstrate the formation of $(CH_3)_4Sn$ from $(CH_3)_3SnOH$ in anaerobic estuarine sediments, but not in seawater and not as surface effects in bentonite. The appearance of $(CH_3)_4Sn$ in both bioactive and sterile sediments suggests the existence of both biotic and abiotic pathways. The abiotic pathway might be similar to that observed with $(CH_3)_3Pb$ salts (11) involving, in this case, the redistribution of $(CH_3)_3SnOH$ to $(CH_3)_4Sn$ and $(CH_3)_2SnO$. However, the reaction with $(CH_3)_3SnOH$ is not catalyzed by sulfide alone, as reported with the lead salts (11).

We have demonstrated the occurrence of a potentially important abiotic pathway for the formation of $(CH_3)_4Sn$ by a Lewis base-induced redistribution of $(CH_3)_3SnOH$. When $(CH_3)_3SnOH$ is treated with sodium thioglycolate in seawater, $(CH_3)_4Sn$ is evolved and a dimethyltin dithioglycolate complex is formed. The dithioglycolate complex of dimethyltin oxide has a metal/ligand ratio of 1/2 and no S-H stretch in the infrared; it is soluble in basic and insoluble in acidic solutions. For this reaction we propose the following mechanism, where L is thioglycolate:



This reaction is interesting because, to our knowledge, it is the first report of a Lewis base-induced redistribution of an organotin compound, although such redistributions have been reported for mercury (3, 12) and lead (11). Further studies are under way to elucidate the mechanism of the organotin redistribution reaction.

We suggest that this pathway may be of considerable importance in explaining the formation of tetraalkyl metal species from trialkyl metal species. The biotic pathway in the case of $(CH_3)_3SnOH$ may include formation of a sulfur-containing ligand that induces this reaction. A similar mechanism is probably responsible for the formation of $(CH_3)_4Pb$ and perhaps other "biomethylations" of methylmetal compounds.

The environmental significance of the formation of $(CH_3)_4Sn$ from the trimethyltin species is probably minor. Our studies show that this reaction occurs in very low yield. Since $(CH_3)_4Sn$ is volatile and water-insoluble, it should not

accumulate in the marine environment but should escape to the atmosphere. The other product, $(CH_3)_2SnX_2$, may be removed from the ecosystem as the very insoluble $(CH_3)_2SnO$ but more likely accumulates in the form of complexes with sulfur-containing ligands found in sediments (13).

Although it is difficult to extrapolate from this investigation of a trimethyltin compound to the fate of the antifouling tributyltin compounds, some inferences may be drawn. Biomethylation of the tributyltins is not likely to be more than a minor process. The postulated redistribution may occur with the tributyltin species being converted to dibutyltins and tetrabutyltin. This possibility should be considered in future investigations of the environmental impact of organotins.

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5. The reduction of trialkyltin(IV) compounds to a nominal tin(III) dimer (R_3SnSnR_3) requires the use of an alkali metal reductant in nonaqueous solution. Even such powerful reducing agents as lithium aluminum hydride and lithium hydride do not reduce trialkyltin(IV) compounds to tin(III) species but form tin(IV) hydrides [G. P. Van der Kelen, E. V. Van den Berghe, L. Verdonck, in *Organotin Compounds*, A. K. Sawyer, Ed. (Dekker, New York, 1971), pp. 81-151]. In view of this chemistry, it is not likely that, in the aqueous medium of an anoxic estuarine sediment, a sufficient reduction potential for formation of a trialkyltin(III) species could be obtained.
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10. The decrease in $(CH_3)_4Sn$ detected in the flask headspace after 70 to 80 days is probably the result of a decreased rate of the $(CH_3)_4Sn$ production combined with absorption of the $(CH_3)_4Sn$ into the rubber stopper or loss due to repeated puncturing of the sampling nipple, or both.
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14. This work was supported by the Office of Naval Research under contract with the Regents of the University of California, Berkeley.

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